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Infrared spectra of charge transfer complexes of bis(N-ethylsalicylaldiminato)Cu^{II}

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Abstract : Charge transfer complexes of bis(N-ethylsalicylaldiminato)Cu^{II} with organic acceptors like TCNQ, TCNE, TNF, DDQ, chloranil and iodine have been prepared and studied with Fourier transform infrared spectroscopy. The electron donating chelate is isostructural to the methyl analog in which metal chains are found in one crystallographic direction. The spectra obtained in the range of 400–4000 cm^{-1} are mainly governed by the donor spectrum. Only above 1700 cm^{-1}, the acceptor bands are visible. DDQ and chloranil both containing chlorine atoms interact more strongly as compared to other acceptors. The electronic absorption envelopes are identified. The nature of transition, band tailing effect and free-carrier absorption are also analyzed. Observed steric effects of ethyl groups compared to methyl groups are discussed.

Keywords : Charge transfer complexes, organic acceptors, infrared spectra, optical conductivity, band assignment

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1. Introduction

Recently, we are studying a series of bis (N-R-salicylaldiminato)M^{II}, where R = H, CH_3, C_2H_5 and C_6H_5 and M^{II} = Ni^{II}, Cu^{II}, because the metal chains were observed in some of them and the materials were found to be anti-ferromagnetic [1,2]. This work was inspired because of the interest in working on quasi-one-dimensional conductors and synthetic metals [3–7] among solid state physicists. A large number of organic CT complexes are known [8–10], but those of organometallic chelates have been limited.

In the persent work, we study infrared spectra of charge transfer complexes bis(N-ethylsalicylal-diminato)Cu^{II} using analysis like nature of transitions above 1700 cm^{-1}, band assignments below 1700 cm^{-1}, free-carrier absorption and band tailing effects.

2. Experimental

Blue-black coloured bis(N-ethylsalicylaldiminato)Cu^{II} was prepared by a reaction of salicyldehyde, ethyl amine, $CuCl_2.2H_2O$ and KOH (a base) with an exothermic reaction. The precipitates were washed with concentrated KOH solution to remove traces of $Cu(OH)_2$. Then, these precipitates were allowed to dry for 3–4 days before grinding to a fine powder in a mortar. The microcrystalline material was crushed and grinded with acceptors like TCNQ (7,7,8,8-tetracyano-p-quinodimethane), TCNE (N,N,N',N'-tetracyanoethylene), TNF (2,4,5,7-tetranitro-9-fluourenone), DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone), chloranil (2,3,5,6-tetrachloro-p-benzoquinone) and iodine. The colour was deepened, became blue and black by the formation of charge transfer complex (Table 1).

The black coloured charge transfer complexes were once more grinded with dry KBr powder to prepare semitransparent pellets for IR measurement by compressing the homogeneous mixture in a die. The FTIR spectra in the range of 400–4000 cm^{-1} were recorded by using GX-FTIR single beam spectrophotometer made by Perkin Elmer Co. USA having a resolution of 0.15 cm^{-1}, scan

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Table 1. Optical and infrared properties of or complexes of Cu(N-C_2H_5-salim)$_2$

Name of the complex	Colour	Absorption function	Nature of transition	Value of Eg (eV)
Cu(N-C_2H_5-salim)$_2$-TCNQ	Greenish-blue	$\alpha h\nu = \alpha_0(h\nu - E_g)^{3/2}$	Direct forbidden	0.206
Cu(N-C_2H_5-salim)$_2$-TCNE	Black	$\alpha h\nu = \alpha_0(h\nu - E_g)^2$	Indirect allowed	0.219
Cu(N-C_2H_5-salim)$_2$-TNF	Brown	$\alpha h\nu = \alpha_0(h\nu - E_g)^3$	Indirect forbidden	0.225
Cu(N-C_2H_5-salim)$_2$-DDQ	Brown	$\alpha h\nu = \alpha_0(h\nu - E_g)^2$	Indirect allowed	0.219
Cu(N-C_2H_5-salim)$_2$-chloranil	Greenish-blue	$\alpha h\nu = \alpha_0(h\nu - E_g)^{1/2}$	Direct allowed	0.225
Cu(N-C_2H_5-salim)$_2$-iodine	Black brown	$\alpha h\nu = \alpha_0(h\nu - E_g)^3$	Indirect forbidden	0.2125

range of 15,600–30 cm^{-1}, scan time 20 scan/sec., OPD velocity 0.20 cm/sec and MIRTGS and FIRTGS detectors were used. Beam splitter used is OptKbr, which has a range of 7800–370 cm^{-1}. The spectra were recorded in the purge mode. Molecular structures of the donor chelate organic acceptors are shown (Figure 1).

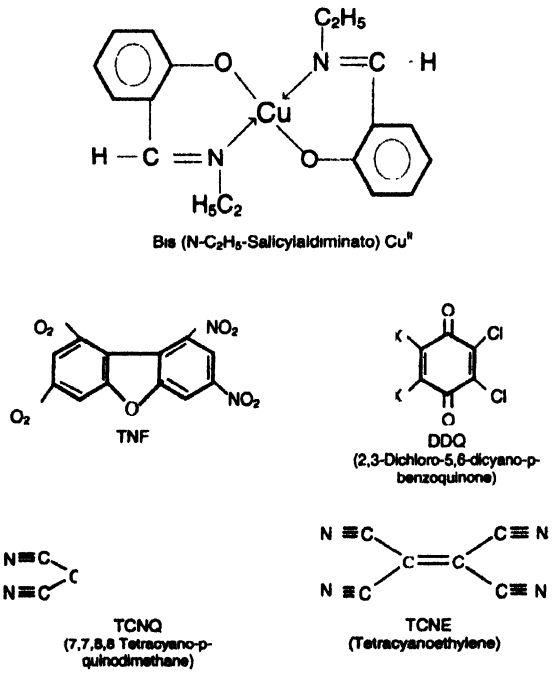

Figure 1. Molecular structure of the donor chelate and organic acceptors.

3. Results and discussion

The infrared spectrum of bis(N-ethylsalicylaldiminato)Cu^{II} is shown (Figure 2) and featureless background absorption is attributed to a permenant dipole moment of the chelate molecule or metal-chain formation in one direction. Band assignments have been carried out (Table 2). There are mainly two absorption envelopes, one around 1470 cm^{-1} and the other around 770 cm^{-1}. These envelopes are associated with the out-of-phase vibrations of two electrons as found in phthalocyanines and porphyrins [11,12].

The infrared spectra of the donor-acceptor complexes of this salicylaldiminato are shown in Figures 3 and 4. There is a featureless background absorption which has been analyzed for either direct or indirect transition (Figure 5 and Table 1).

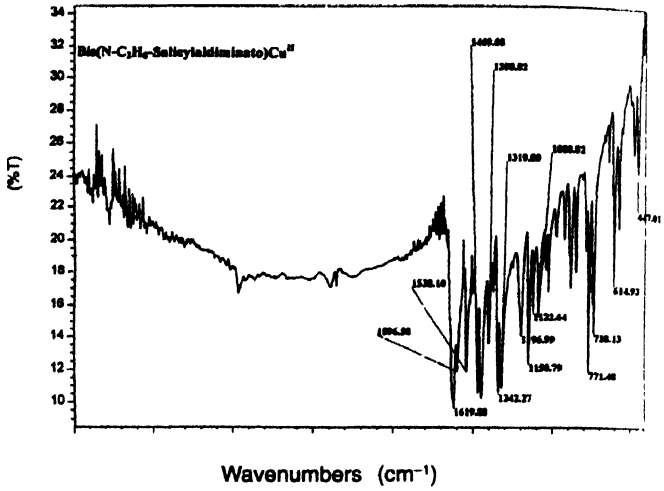

Figure 2. Infrared spectrum of bis(N-ethylsalicylaldiminato)Cu^{II}.

Table 2. Band assignments in the IR spectrum of bis(N-C_2H_5-salicylaldiminato)Cu^{II}.

Wave number (cm^{-1})	Band assignments
1620	δ_{N-H}
1597	$\nu_{C=N}$ (Un sym)
1538	$\nu_{C=N}$ (sym)
1470	δ_{C-H}
1342	ν_{C-O}
1320	ν_{C-O}
1197	ν_{C-N}
1151	New band
1123	ν_{C-C}
1089	ν_{C-C}
771	π_{C-H}
738	π_{C-H}
614	M–L
447	M–L

The absorption changes monotonically with frequency according to

$$\alpha h\nu = B(h\nu - Eg)^r,$$

where Eg being the energy gap, where r = 1/2 for allowed direct transition, r = 3/2 for forbidden direct transition, r = 2 for allowed indirect transition and r = 3

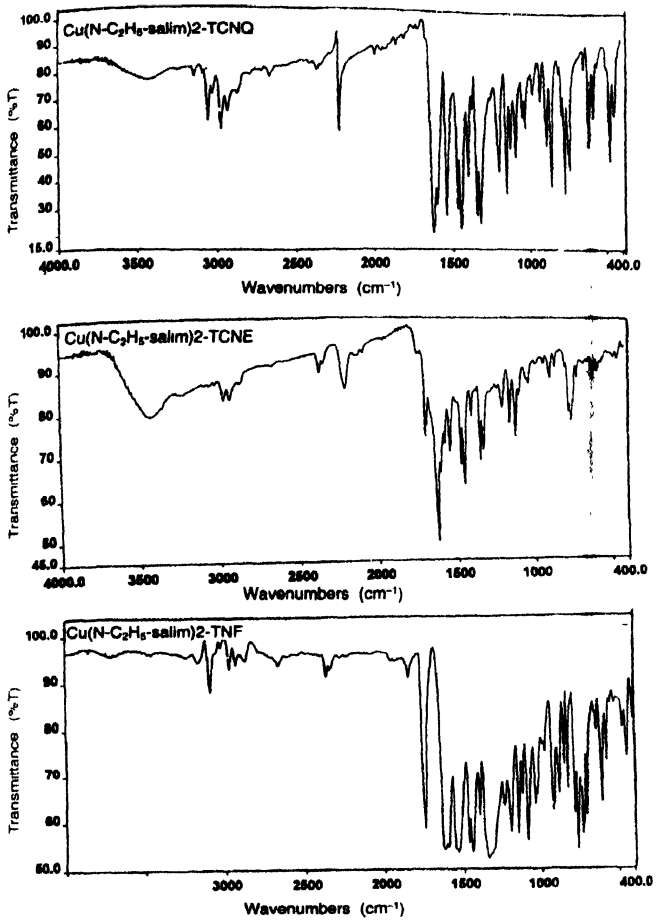

Figure 3. Infrared spectra of (a) Cu(N-C_2H_5-Salim)$_2$-TCNQ, (b) Cu(N-C_2H_5-Salim)$_2$-TCNE and (c) Cu(N-C_2H_5-Salim)$_2$-TNF.

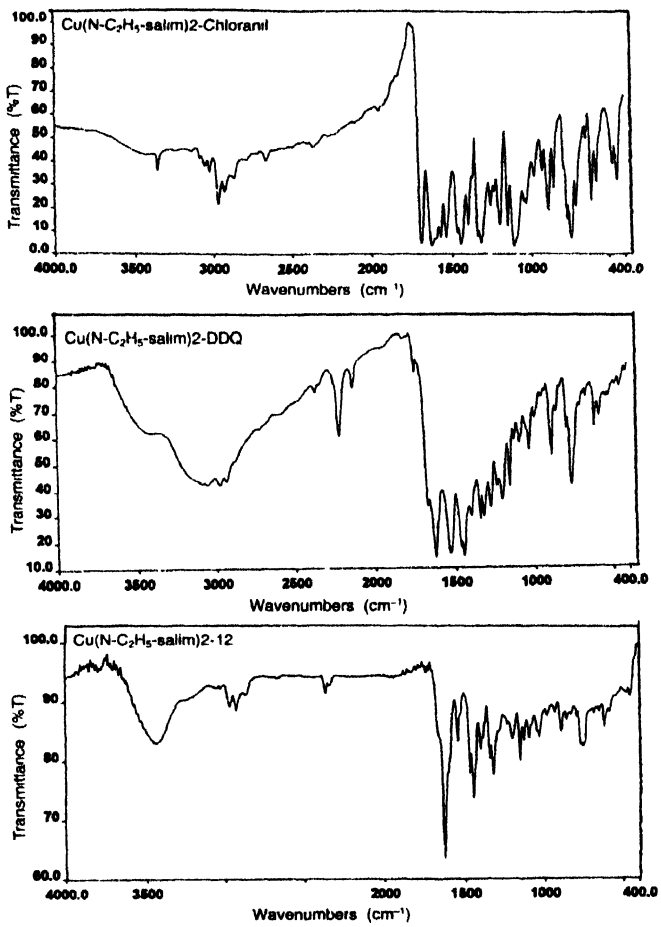

Figure 4. Infrared spectra of (a) Cu(N-C_2H_5-Salim)$_2$-chloranil, (b) Cu(N-C_2H_5-Salim)$_2$-DDQ and (c) Cu(N-C_2H_5-Salim)$_2$-I_2.

for forbidden indirect transition. When the material is crystalline, it obeys

$$\alpha = B(h\nu - Eg)^{r}.$$

Here, it is considered that the material is inhomogeneous and disordered, so $(\alpha h\nu)^{1/r}$ *vs.* $h\nu$ has been plotted (Figure 5). In TCNQ and chloranil complexes, a direct transition is found, in TNF and iodine complexes a forbidden indirect transition is found and in DDQ and TCNE complexes an allowed indirect transition is observed.

Apart from this, at somewhat lower wave numbers in DDQ and TCNE complexes, the absorption envelopes are found to be asymmetric. Gaussian or Lorentzians (Table 3) symmetric envelopes are found in TCNQ, TNF, and chloranil complexes. Envelope is a modulation by intramolecular vibrational band which appears as its fine structure. Background absorption is pronounced in TNF, DDQ and chloranil complexes. Absolute absorption and reflection are much more in DDQ and chloranil complexes

Table 3. Details of absorption envelopes.

Name of the complex	High frequency envelope			Low frequency envelope		
	Intensity *A*	K_{max} (cm^{-1})	Full-width at half maximum (*G*/*L*)	Intensity *A*	K_{max} (cm^{-1})	Full width at half maximum (*G*/*L*)
Cu(N-C_2H_5-Salim)$_2$-TCNQ	80	1500	600 (G)	60	771	250 (G)
Cu(N-C_2H_5-Salim)$_2$-TCNE	50	1623	350 (L)	22	754	250 (L)
Cu(N-C_2H_5-Salim)$_2$-TNF	48	1347	700 (G)	45	770	300 (G)
Cu(N-C_2H_5-Salim)$_2$-DDQ	85	1524	500 (G)	55	764	400 (G)
Cu(N-C_2H_5-Salim)$_2$-chloranil	98	1400	700 (G)	90	747	300 (L)
Cu(N-C_2H_5-Salim)$_2$-iodine	85	1300	500 (G)	87	700	250(G)

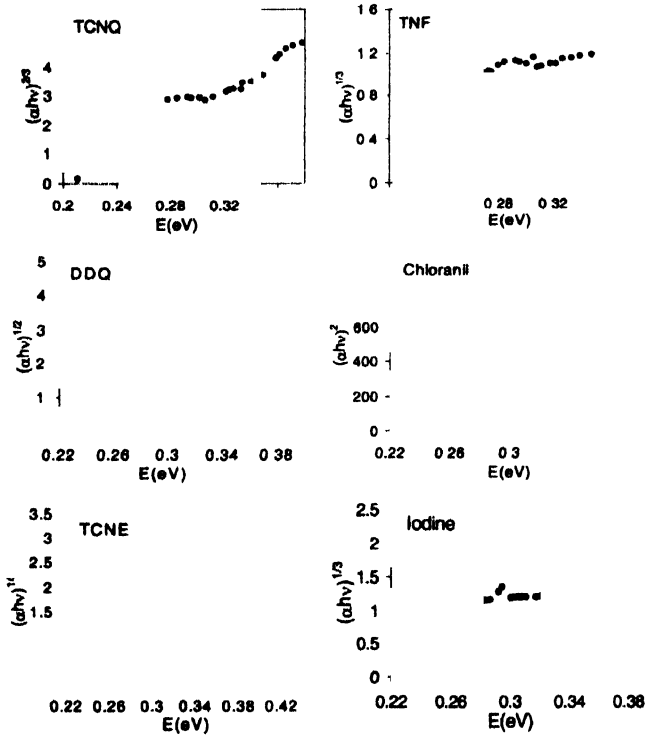

Figure 5. Nature of transition in the charge transfer complexes of Cu(N-C_2H_5-Salim)$_2$.

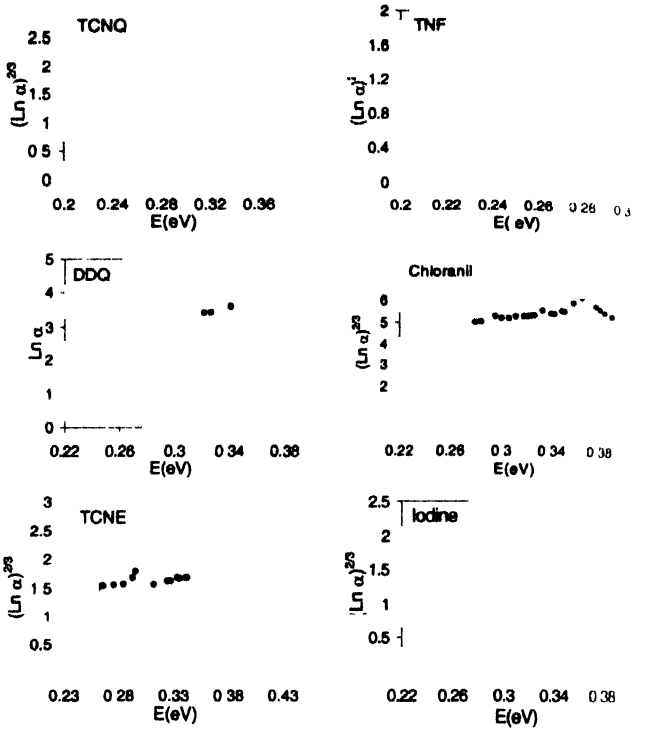

Figure 6. Band tailing in the charge transfer complexes of Cu(N-C_2H_5-Salim)$_2$

compared to other complexes. Reflection and absorption spectra are governed by each other [13]. Thus, a transmission dip can appear as peaks in both absorption and reflectance. In chloranil complex, the peak in the range of 1700–1100 cm^{-1} is a flat peak as can be obtained by joining transmission dips. Thus, the charge density waves are trapped in a rectangular potential well which do not tunnel because of weak dipolar field of symmetric chloranil molecule. In DDQ complex, there is tunneling indicated by an asymmetric Gaussian shape in this range.

Band tailing effects are also analyzed by studying the higher wavenumber edge of background having featureless absorption (Figure 6). The band tailing is described by,

$$\alpha = \alpha_0 \exp\left(\frac{h\nu - E_1}{E_0}\right),$$

and consequently the width of the tail E_0 is described by

$$E_0 = \left(\frac{d\ln\alpha}{d\nu}\right)^{-1}.$$

Thus, ln α *vs* $h\nu$ is plotted to fit a straight line (Figure 6). When the internal electric field leads to tunneling of charge carriers, it obeys the equation of internal Franz-Keldysh effect as [14],

$$\alpha = \alpha_0 \exp\left(\frac{h\nu - E_g}{E_0}\right)^{3/2}$$

Thus, $(\ln\alpha)^{2/3}$ *vs.* $h\nu$ should be a straight line. This type of behaviour is observed in the present study in the cases of TCNQ, TCNE, TNF, chloranil and iodine complexes Only in DDQ complex, an Urbach tail is found which is an exponentially falling absorption edge. Normal Urbach tail reveals crystalline materials.

Free carrier absorption described by $\alpha_f = A\lambda^{1.5} + B\lambda^{2.5} + C\lambda^{3.5}$ is also analyzed to see whether scattering of charge carriers occur by acoustic phonons, optical phonons or ionized impurities [15,16]. For this, log λ *vs* log α are plotted (Figure 7) considering one of the mechanisms of scattering being pre-dominant. If the slope of the graph of log α *vs.* log λ is 1.5, acoustic phonons scatter, if it is 2.5, optical phonons scatter and if it is 3.5, ionized impurities scatter. Here, except the chloranil complex (where this slope is 1.3), the slope is about 3.8 to 4.0 revealing that ionized impurities scatter charge carriers. Only in the chloranil complex where charge transfer binding is maximum, acoustic phonons scatter. The accepter counter-ions located at the defect and disordered sites act as impurities in all other complexes. This can be related with steric effects (stereo-chemical effect) of the ethyl gropus in bis(N-ethylsalicylaldiminato)Cu^{II}.

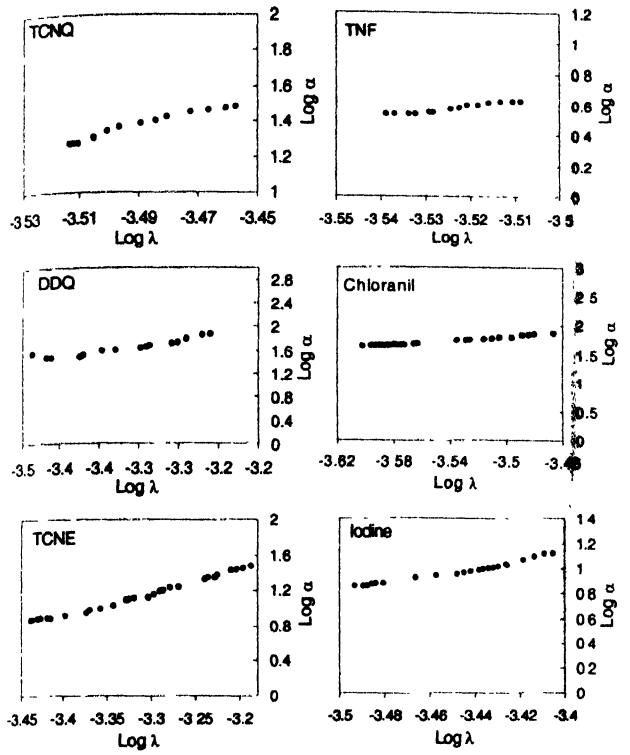

Figure 7. logα *vs.* logλ for free-carrier absorption in the charge transfer complexes of Cu(N-C_2H_5.Salim)$_2$.

Band assignments of charge transfer complexes are also carried out (Tables 4 and 5). The plot of $\ln\sigma_{max}$ *vs.* n, where σ_{max} is the maximum optical conductivity and n is the number of bands in the envelope is plotted (Figure 8 and Table 6). Optical conductivity increases with the number of vibrational modes which couple with charge carriers and reveals delocalization effects of intramolecular vibrations.

Table 4. Band assignments in the IR spectra of CT complexes of Cu(N-C_2H_5-Salim)$_2$.

Cu(N-C_2H_5-Salim)$_2$-TCNQ		Cu(N-C_2H_5-Salim)$_2$-TCNE		Cu(N-C_2H_5-Salim)$_2$-TNF	
Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment
3050	ν_{C-H}	3425	ν_{N-H}	3088	ν_{N-H}
2969	$\nu_{C\equiv N}$	2931	$\nu_{C\equiv N}$	2968	ν_{C-H}
2927	$\nu_{C\equiv N}$	2356	$\nu_{C\equiv N}$	1740	ν_{C-O}
2222	$\nu_{C\equiv N}$	2292	$\nu_{C\equiv N}$	1622	δ_{N-H} or ν_{NO_2}
1622	δ_{N-H}	1691	ν_{C-N}	1536	$\nu_{C=C}$
1539	$\nu_{C=N}$	1623	δ_{N-H}	1401	δ_{NO_2}
1408	δ_{C-H}	1470	ν_{C-C}	1345	ν_{C-O}
1321	ν_{C-O}	1449	δ_{C-H}	1197	ν_{C-N}
1197	ν_{C-C}	1400	δ_{C-H}	1150	ν_{C-N}
1150	ν_{C-N}	1343	ν_{C-O}	1090	ν_{C-C}
1123	ν_{C-C}	1323	ν_{C-O}	1041	ν_{C-C}

Table 4. *Cont'd.*

1089	ν_{C-C}	1197	ν_{C-N}	925	ν_{C-NO_2}
1027	ν_{C-C}	1150	ν_{C-N}	888	ν_{C-NO_2}
928	ν_{C-C}	1113	ν_{C-C}	770	π_{C-H}
888	ν_{C-C}	1025	ν_{C-C}	736	π_{C-H}
859	ν_{C-C}	888	π_{C-H}	709	π_{C-H}
771	π_{C-H}	753.5	π_{C-H}	610	M-L
738	π_{C-H}	604	M-L	576	M-L
642	π_{C-H}			448	M-L
610	π_{C-H}				
576	M-L				
474	M-L				

Table 5. Band assignments in the IR spectra of CT complexes of Cu(N-C_2H_5-Salim)$_2$.

Cu(N-C_2H_5-Salim)$_2$-DDQ		Cu(N-C_2H_5-Salim)$_2$-chloranil		Cu(N-C_2H_5-Salim)$_2$-I_2	
Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment
3051	ν_{N-H}	3356	ν_{N-H}	3440	ν_{N-H}
2219	$\nu_{C\equiv C}$	3023	ν_{C-H}	2967	ν_{C-H}
2135	New band	2968	$\nu_{C\equiv N}$	2925	ν_{C-H}
1622	δ_{N-H}	1686	δ_{N-H}	2358	$\nu_{C\equiv N}$
1534	$\nu_{C=N}$	1622	δ_{N-H}	1621	δ_{N-H}
1451	δ_{C-H}	1537	ν_{C-N}	1538	$\nu_{C=N}$
1321	ν_{C-O}	1446	δ_{C-H}	1447	δ_{C-H}
1276	ν_{C-C}	1320	ν_{C-O}	1322	ν_{C-O}
1201	ν_{C-N}	1258	ν_{C-N}	1196	ν_{C-C}
1151	ν_{C-O}	1198	ν_{C-N}	1149	ν_{C-N}
1100	ν_{C-N}	1110	ν_{C-C}	1123	ν_{C-N}
1027	ν_{C-C}	928	π_{C-H}	1027	ν_{C-C}
886	π_{C-H}	886	π_{C-H}	888	ν_{C-C}
764	ν_{C-Cl}	854	π_{C-H}	748	π_{C-H}
609	M-L	747	ν_{C-Cl}	640	Group vib.
		711	ν_{C-Cl}		
		608	Group vib.		
		575	M-L		
		472	M-L		
		443	M-L		

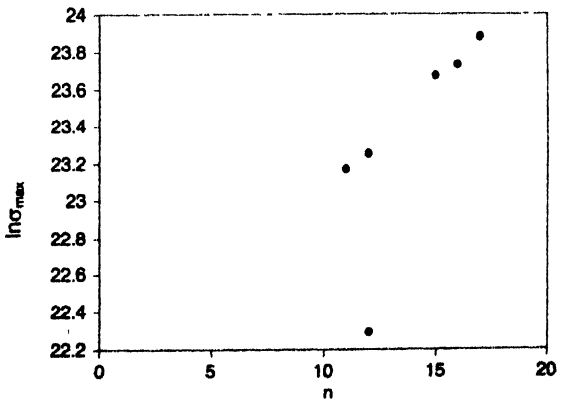

Figure 8. ln σ_{max} *vs.* n where σ_{max} is the maximum optical conductivity and n is the no. of bands in the envelope.

Table 6. Dependence of absorption function on dimensionality $\alpha = \alpha_0 \frac{(h\nu - Eg)^r}{h\nu}$ values of exponent r for different types of transitions across the band gap.

Type of transition	Direct			Indirect		
	One dimention	Two dimention	Three dimention	One dimention	Two dimention	Three dimention
Allowed	1/2	0	1/2	2	1	2
Forbidden	3/2	1	3/2	3	2	3

$\alpha = \alpha_0 (h\nu - Eg)^r$ for the crystalline materials with same r values.

Table 7. $\ln\sigma_{max}$ *vs. n*.

Name of the complex	Transmission %	Absorbance Arb. Units %	$\sigma = \frac{\alpha n_1 C'}{4\pi}$ 10^{10} sec^{-1}	$\ln\sigma_{max}$	*n* no. of bands in envelope
Cu(N-C_2H_5-Salim)$_2$-TCNQ	20	80	1.91	23.67	15
Cu(N-C_2H_5-Salim)$_2$-TNF	52	48	1.15	23.17	11
Cu(N-C_2H_5-Salim)$_2$-DDQ	15	85	2.03	23.73	16
Cu(N-C_2H_5-Salim)$_2$-chloranil	2	98	2.34	23.88	17
Cu(N-C_2H_5-Salim)$_2$-TCNE	47.5	52.5	1.25	23.25	12
Cu(N-C_2H_5-Salim)$_2$-I_2	80	20	0.48	22.29	12

4. Conclusion

The infrared spectra of the charge transfer complexes of bis(N-ethylsalicylaldiminato)Cu^{II} are studied. Absorption bands can describe steric effects of ethyl groups around 2900 or 3000 cm^{-1} range which are not seen in the methyl analogs. Free electronic motions are hindered by sterically hindering ethyl groups. Also ethyl groups lead to overall steric effects of a non-planar molecule. The nitrogen atom gets quaternized by methyl group and gets positively charged but here in ethyl - based chelate, this quaternization effect is reduced by steric hindrance.

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